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POSITIVE ELECTRODE FOR LITHIUM-SULFUR BATTERY AND LITHIUM-SULFUR BATTERY COMPRISING SAME

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority to application No. 2002-73961 filed in the Korean Intellectual Property Office on November 26, 2002, the disclosure of which is incorporated hereinto by reference.

FIELD OF THE INVENTION

The present invention relates to a positive electrode for a lithium-sulfur battery and a lithium-sulfur battery comprising the same, and more particularly, to a positive electrode for a lithium-sulfur battery exhibiting good cycle life characteristics.

BACKGROUND OF THE INVENTION

The continued development of portable electronic devices has led to a corresponding increase in the demand for secondary batteries having both a lighter weight and a higher capacity. To satisfy these demands, the most promising approach is a lithium-sulfur battery with a positive electrode made of sulfur-based compounds.

Lithium-sulfur batteries use sulfur-based compounds with sulfur-sulfur bonds as a positive active material, and a lithium metal or a carbon-based compound as a negative active material. The carbon-based compound is one that can reversibly intercalate or deintercalate metal ions, such as lithium ions. Upon discharging (i.e., electrochemical reduction), the sulfur-sulfur bonds are cleaved, resulting in a decrease in the oxidation number of sulfur (S). Upon recharging (i.e., electrochemical oxidation), the sulfur-sulfur bonds are re-formed, resulting in an increase in the oxidation number of the S. The electrical energy is stored in the battery as chemical energy during charging, and is converted back to electrical energy during discharging.

With respect to specific density, the lithium-sulfur battery is the most attractive among the currently developing batteries since lithium has a specific capacity of 3,830 mAh/g, and sulfur has a specific capacity of 1,675 mAh/g. Further, the sulfur-based compounds are less costly than other materials, and they are environmentally friendly.

However, employing a positive electrode based on elemental sulfur in an alkali metal-sulfur battery system has been considered problematic. Although theoretically the reduction of sulfur to an alkali metal-sulfide confers a large specific energy, sulfur is known to be an excellent insulator, and problems using it for an electrode have been noted. Such problems

include a very low percentage of utilization and low cycle life characteristics as a result of the sulfur and lithium sulfide (Li_2S) dissolving and diffusing from the positive electrode.

Thus, there have been various studies to improve the electrochemical redox reaction and to increase capacity.

SUMMARY OF THE INVENTION

The present invention provides a positive electrode for a lithium-sulfur battery exhibiting good cycle life characteristic by controlling the roughness of the surface of the positive electrode using an additive with a critical particle size.

In one embodiment, the invention is directed to a positive electrode for a lithium-sulfur battery including a positive active material selected from elemental sulfur (S_8), a sulfur-based compound, or a mixture thereof; a conductive material; a binder; and an inorganic additive that is soluble in an electrolyte. The inorganic additive may be a metal oxide, a metal sulfide, or a mixture thereof. The particle size can be suitably controlled depending on the type of metal in the inorganic additive. If the metal is V, Zr, Al, or Ti, the particle size D (v, 50%) is preferably 5,000 nm or less.

The present invention also provides a lithium-sulfur battery including the positive electrode, a negative electrode and an electrolyte. The negative electrode includes a negative active material selected from a material that is capable of reversibly intercalating or deintercalating lithium ions, a material that reacts with lithium ions to prepare a lithium-included compound, a lithium metal, and a lithium alloy.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention, and many of the attendant advantages thereof, will be readily apparent as the same becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings, wherein:

FIG. 1 is a drawing illustrating immersion of a positive electrode for a test;

FIG. 2 is an SEM photograph of an electrode obtained from a lithium-sulfur cell according to Example 1 of the present invention after 10 charge and discharge cycles;

FIG. 3 is a drawing illustrating a collected portion of a sample of the electrode used for measuring the particle size of an additive; and

FIG. 4 is a drawing illustrating a lithium-sulfur battery of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Reference will now be made in detail to the present preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawings, wherein like reference numerals refer to like elements throughout. The embodiments are described below in order to explain the present invention while referring to the figures.

The present invention relates to a positive electrode for a lithium-sulfur battery using an inorganic additive with a desired particle size, and that is insoluble in an electrolyte. The positive electrode can provide batteries exhibiting good cycle life characteristics.

Such an inorganic additive includes metal oxides, metal sulfides or a mixture thereof. Exemplary metals include V, Al, Zr, and Ti. Preferred are V_2O_5, Al_2O_3, ZrO_2, and TiS_2.

The preferred particle size of the inorganic additive depends on the type of metal, that is, the type of inorganic additive. If a V_2O_5, Al_2O_3, ZrO_2, or TiS_2 additive is used, the particle size D (v, 50%) is preferably 5,000 nm or less, more preferably from 1 to 5,000 nm, even more preferably from 5 to 4,000 nm, and still more preferably from 10 to 3,000 nm. In this application, the term "particle size D (v, 50%)" means a particle size in which particles distributed with various size such as 0.1, 0.2, 0.3 .... 3, 5, 7, ...10, 20, or 30μm are accumulated to 50 volume %. As the particle size D (v, 50%) decreases, ionic conductivity increases so that a small particle size is preferable. If the particle size D (v, 50%) is out of the range, the surface roughness (Ra) of a produced positive electrode increases, making the surface of the positive electrode uneven, thereby deteriorating the capacity and particularly cycle life characteristics.

The particle size of the inorganic additive may be controlled by a general mechanically mixing process such as a ball-milling process. The metal oxide or metal sulfide is pulverized in a solvent with a zirconia ball for 3 to 24 hours. If the pulverizing step is performed for less than 3 hours, desired particle sizes cannot be obtained. The particle size obtained from the pulverizing step for 24 hours is substantially the minimum size, so it is not required to perform the pulverizing step beyond this time. The solvent is any solvent that does not react with the metal oxide or metal sulfide, and useful solvents include isopropyl alcohol, ethyl alcohol, and methyl alcohol.

The additive with the above particle size renders a decrease in the average surface roughness Ra of 5 μm. Such a decreased surface roughness allows a decrease in interfacial resistance between a positive electrode and a separator, thereby decreasing internal resistance of batteries and providing good battery performance.

The present invention improves battery performance by controlling particle size of the inorganic additive. Studies on the specific effect of particle size on the battery performances have not been undertaken. For example, U.S. Patent Nos. 6,238,821 and 6,210,831 disclose the use of a V_2O_5 additive in a positive electrode, and U. S. Patent Nos. 6,238,821, 6,406,814 and 6,210,831 disclose the use of Al_2O_3 in a positive electrode. However, these patents are silent on control of the particle size of V_2O_5 and Al_2O_3. In addition, U.S. Patent No. 6,130,007 discloses a vanadium oxide positive active material with a particle size of 1000 nm or less, but this did not exhibit suitable capacity and cycle life. U.S. Patent No. 5,474,858 discloses a positive electrode with an alumina drying agent, but is silent on the particle size of alumina. U.S. Patent No. 5,360,686 discloses alumina with a particle size of 0.5 micrometer. This patent uses alumina in order to increase the mechanical strength of an electrolyte, but it is silent regarding alumina with a suitable particle size being capable of decreasing internal resistance of the battery. Thus, it is well understood to one in the related art that the battery performance improvement effect of the present invention by using an additive with a critical particle size cannot be obtained from these cited references.

The positive electrode of the present invention includes the additive as well as a positive active material, a conductive material, and a binder.

The positive active material includes elemental sulfur (S_8), a sulfur-based compound, or a mixture thereof. The sulfur-based compound may be selected from Li_2S_n ($n \geq 1$), organic-sulfur compounds, and carbon-sulfur polymers ($(C_2S_x)_n$: $x= 2.5$ to 50, $n \geq 2$).

The conductive material includes an electrically conductive material that facilitates the movement of electrons within the positive electrode. Examples of the conductive material include, but are not limited to, conductive materials such as graphite- and carbon-based materials, and conductive polymers. The graphite-based materials include KS 6 (manufactured by TIMCAL COMPANY), and the carbon-based materials include SUPER P (manufactured by MMM COMPANY), ketjen black, denka black, acetylene black, carbon black, and the like. Examples of the conductive polymer include, but are not limited to, polyaniline, polythiophene, polyacetylene, polypyrrole, and the like. The conductive material may be used alone or as a mixture of two or more of the above conductive materials.

A binder may be added to adhere the positive active material on a current collector. The binder may be poly(vinyl acetate), polyvinyl alcohol, polyethylene oxide, polyvinyl pyrrolidone, alkylated polyethylene oxide, crosslinked polyethylene oxide, polyvinyl ether, poly(methyl methacrylate), polyvinylidene fluoride, a copolymer of polyhexafluoropropylene and polyvinylidene fluoride (Trademark: KYNAR), polyethyl acrylate, polytetrafluoroethylene,

polyvinyl chloride, polyacrylonitrile, polyvinyl pyridine, polystyrene, a derivative thereof, a blend thereof, or a copolymer thereof.

The positive electrode may further include a coating layer including a polymer, an inorganic material, or a mixture thereof.

The polymer may include polyvinylidene fluoride, a copolymer of polyvinylidene fluoride and hexafluoropropylene, poly(vinyl acetate), poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate), poly(methylmethacrylate-co-ethyl acrylate), polyacrylonitrile, polyvinyl chloride-co-vinyl acetate, polyvinyl alcohol, poly(1-vinylpyrrolidone-co-vinyl acetate), cellulose acetate, polyvinyl pyrrolidone, polyacrylate, polymethacrylate, polyolefin, polyurethane, polyvinyl ether, acrylonitrile-butadiene rubber, styrene-butadiene rubber, acrylonitrile-butadiene styrene, a sulfonated styrene/ethylene-butylene/styrene triblock copolymer, polyethylene oxide, or a mixture thereof.

Examples of inorganic material include colloidal silica, amorphous silica, surface-treated silica, colloidal alumina, amorphous alumina, tin oxide, titanium oxide, titanium sulfide (TiS_2), vanadium oxide, zirconium oxide (ZrO_2), iron oxide, iron sulfide (FeS), iron titanate ($FeTiO_3$), barium titanate ($BaTiO_3$), and mixtures thereof. The organic material may be conductive carbon.

The positive electrode of the present invention is produced by the general procedure in which the positive active material, the conductive material, the binder, and the inventive inorganic additive are mixed in a solvent to prepare a composition (e. g. in the form of slurry), and the composition is coated on a current collector.

A lithium-sulfur battery of the present invention with the positive electrode includes a negative electrode and an electrolyte. An embodiment of a lithium-sulfur battery 1 of the present invention is shown in FIG. 4. The lithium-sulfur battery 1 in FIG. 4 includes the positive electrode 3, a negative electrode 4, and a separator 2 interposed between the positive electrode 3 and the negative electrode 4. The positive electrode 3, the negative electrode 4, and the separator 2 are received in a battery case 5. The electrolyte is present between the positive electrode 3 and the negative electrode 4.

The negative electrode of the lithium-sulfur battery includes a negative active material selected from materials in which lithium intercalation reversibly occurs, materials that react with lithium ions to form a lithium-containing compound, lithium metals, and lithium alloys.

The materials in which lithium intercalation reversibly occurs include carbon-based compounds. Any carbon-based compound may be used as long as it is capable of intercalating

and deintercalating lithium ions. Examples of such carbon materials include crystalline carbon, amorphous carbon, and mixtures thereof.

Examples of the material that reacts with lithium ions to form a lithium-containing compound include, but are not limited to, tin oxide (SnO_2), titanium nitrate, and Si. The lithium alloys include alloys of lithium and a metal selected from Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Al, and Sn.

The negative electrode may include an inorganic protective layer, an organic protective layer, or a mixture thereof, on a surface of lithium metal. The inorganic protective layer includes Mg, Al, B, Sn, Pb, Cd, Si, In, Ga, lithium silicate, lithium borate, lithium phosphate, lithium phosphoronitride, lithium silicosulfide, lithium borosulfide, lithium aluminosulfide, or lithium phosphosulfide. The organic protective layer includes a conductive monomer, oligomer, or polymer selected from poly(p-phenylene), polyacetylene, poly(p-phenylene vinylene), polyaniline, polypyrroloe, polythiophene, poly(2,5-ethylene vinylene), acetylene, poly(perinaphthalene), polyacene, and poly(naphthalene-2,6-di-yl).

In addition, during charging and discharging of the lithium-sulfur battery, the positive active material (active sulfur) converts to an inactive material (inactive sulfur), which can be attached to the surface of the negative electrode. The term "inactive sulfur", as used herein, refers to sulfur that has no activity upon repeated electrochemical and chemical reactions so it cannot participate in an electrochemical reaction of the positive electrode. The inactive sulfur on the surface of the negative electrode acts as a protective layer of the lithium negative electrode. Accordingly, inactive sulfur, for example lithium sulfide, on the surface of the negative electrode can be used in the negative electrode.

The electrolyte includes an electrolytic salt and an organic solvent.

The organic solvent may be a sole solvent or a mixed organic solvent with at least two components. The mixed organic solvent includes at least two groups selected from weak polar solvent groups, strong polar solvent groups, and lithium protection groups.

The term "weak polar solvent", as used herein, is defined as a solvent that is capable of dissolving elemental sulfur and has a dielectric coefficient of less than 15. The weak polar solvent is selected from aryl compounds, bicyclic ether, and acyclic carbonate compounds. The term "strong polar solvent", as used herein, is defined as a solvent that is capable of dissolving lithium polysulfide and has a dielectric coefficient of more than 15. The strong polar solvent is selected from bicyclic carbonate compounds, sulfoxide compounds, lactone compounds, ketone compounds, ester compounds, sulfate compounds, and sulfite compounds. The term "lithium protection solvent", as used herein, is defined as a solvent that forms a good protective layer,

i.e. a stable solid-electrolyte interface (SEI) layer, on a lithium surface, and which shows a cyclic efficiency of at least 50%. The lithium protection solvent is selected from saturated ether compounds, unsaturated ether compounds, and heterocyclic compounds including N, O, and/or S.

Examples of the weak polar solvents include xylene, dimethoxyethane, 2-methyltetrahydrofuran, diethyl carbonate, dimethyl carbonate, toluene, dimethyl ether, diethyl ether, diglym, and tetraglyme.

Examples of the strong polar solvents include hexamethyl phosphoric triamide, γ-butyrolactone, acetonitrile, ethylene carbonate, propylene carbonate, N-methyl pyrrolidone, 3-methyl-2-oxazolidone, dimethyl formamide, sulfolane, dimethyl acetamide, dimethyl sulfoxide, dimethyl sulfate, ethylene glycol diacetate, dimethyl sulfite, and ethylene glycol sulfite.

Examples of the lithium protection solvents include tetrahydrofuran, 1,3-dioxolane, 3,5-dimethylisoxazole, 2,5-dimethyl furan, furan, 2-methyl furan, 1,4-oxane, and 4-methyldioxolane.

Examples of electrolyte salts include lithium trifluoromethane sulfonimide, lithium triflate, lithium perchlorate, $LiPF_6$, $LiBF_4$, tetraalkylammonium salts, such as tetrabutylammonium tetrafluoroborate ($TBABF_4$), liquid state salts at room temperature, *e.g.* imidazolium salts such as 1-ethyl-3-methylimidazolium Bis-(perfluoroethyl sulfonyl) imide (EMIBeti), and combinations thereof.

The following examples illustrate the present invention in further detail, but it is understood that the present invention is not limited by these examples.

Example 1

V_2O_5 powder was pulverized in an isopropyl alcohol solvent with a zirconia ball for 3 hours, and the resulting material was dried at 80°C to prepare a V_2O_5 additive with a particle size D (v, 50%) of 5,000 nm.

The V_2O_5 additive, an elemental sulfur (S_8) positive active material, a carbon conductive material, and a polyethyleneoxide binder were mixed in an acetonitrile solvent in the weight ratio of 1 : 6 : 2 : 2 with a ball to prepare a positive active material slurry. The elemental sulfur (S_8) was obtained from pulverization with a zirconia ball in an isopropylalcohol solvent and drying, and it had a particle size D (v, 50%) of 5,000 nm.

The positive active material slurry was coated on a carbon-coated Al current collector to produce a positive electrode for a lithium-sulfur battery.

Example 2

A positive electrode was produced by the same procedure as in Example 1, except that the pulverization step was performed for 6 hours to prepare a V_2O_5 additive with a particle size D (v, 50%) of 200 nm.

Example 3

A positive electrode was produced by the same procedure as in Example 1, except that the pulverization step was performed for 12 hours to prepare a V_2O_5 additive with a particle size D (v, 50%) of 50 nm.

Example 4

A positive electrode was produced by the same procedure as in Example 1, except that the pulverization step was performed for 24 hours to prepare a V_2O_5 additive with a particle size D (v, 50%) of 10 nm.

Example 5

A positive electrode was produced by the same procedure as in Example 1, except that the pulverization step was performed for 1 hour to prepare a V_2O_5 additive with a particle size D (v, 50%) of 30,000 nm.

Example 6

A positive electrode was produced by the same procedure as in Example 1, except that the V_2O_5 additive with a particle size D (v, 50%) of 150,000 nm without a pulverization step was used.

Comparative Example 1

A positive electrode was produced by the same procedure as in Example 1, except that a V_2O_5 additive was not used.

< Experiment 1: Measurement of ionic conductivity according to a particle size D (v, 50%) of V_2O_5>

Polyethylene oxide with a molecular weight of 5,000,000 was dissolved in acetonitrile, and a $LiN(SO_2CF_3)_2$ lithium salt was added thereto and dissolved therein until the mole ratio of ethylene oxide to Li reached 10 : 1. The V_2O_5 additive according to Examples 1 to 7 was added to the resulting solution in an amount of 10 wt% based on the total amount of polyethylene oxide and the $LiN(SO_2CF_3)_2$ lithium salt, and they were shaken for 2 hours. The resulting solution was cast to form a polymer film, and the ionic conductivity thereof was measured. The results are presented in Table 1.

Table 1

Type of polymer film	Ionic conductivity (S/cm) (room temperature)
PEO_{10}-$LiN(SO_2CF_3)_2$	9.6×10^{-7}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5(D(v, 50%)=150,000nm)	1.0×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5(D(v, 50%)=30,000nm)	2.5×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5(D(v, 50%)=5,000nm)	4.5×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5(D(v, 50%)=200nm)	8.6×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5(D(v, 50%)=50nm)	3.0×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5(D(v, 50%)=10nm)	5.0×10^{-5}

As shown in Table 1, the addition of V_2O_5 increased ionic conductivity, and such an increase in ionic conductivity is improved as the particle size of V_2O_5 decreases. This believed to be because the inorganic additive such as V_2O_5 prevents crystallization of the polymer.

Increases in ionic conductivity according to the amount of V_2O_5 were measured. The V_2O_5 with a particle size D (v, 50%) of 10 nm was used. The results are presented in Table 2.

Table 2

Type of polymer film	Ionic conductivity (S/cm)(room temperature)
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5 (2 wt%)	1.0×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5 (5 wt%)	4.0×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5 (10 wt%)	5.0×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5 (15 wt%)	3.5×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5 (20 wt%)	2.0×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-V_2O_5 (25 wt%)	8.0×10^{-6}

It is evident from Table 2 that the amount of 5 to 15 wt% of V_2O_5 exhibited higher ionic conductivity.

These two test results indicate that V_2O_5 increases ionic conductivity, and as the particle size of V_2O_5 decreases, ionic conductivity increases.

< Experiment 2: Measurement of surface roughness>

The surface roughness Ra of the positive electrodes according to Examples 1 to 6 and Comparative Example 1 were measured, and the results are shown in Table 3. Table 3

	Composition of the positive electrode (weight ratio)	Surface roughness (Ra in μm)
Comparative Example 1	Sulfur/Conductive material/Binder (6/2/2)	3.0
Example 6	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=150,000nm) (6/2/2/1)	12.6
Example 5	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=30,000nm) (6/2/2/1)	6.6
Example 1	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=5,000nm) (6/2/2/1)	3.0
Example 2	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=200nm) (6/2/2/1)	2.9
Example 3	Sulfur/Conductive material/Binder /V_2O_5(A: D(v, 50%)=50nm) (6/2/2/1)	2.8
Example 4	Sulfur/Conductive material/Binder /V_2O_5(A: D(v, 50%)=10nm) (6/2/2/1)	2.5

In Table 3, Ra indicates the arithmetic mean of each peak (between highest and lowest peaks), and the lower Ra indicates a more uniform surface. It is evident from Table 3 that Examples 5 and 6 with the particle size of V_2O_5 larger than the sulfur active material (5,000 nm) exhibited poorer uniformity (unevenness and roughness) than Comparative Example 1 without V_2O_5, and Examples 1 to 4 with a smaller or the same particle size of V_2O_5 as the active material exhibited substantially the same or better uniformity.

< Experiment 3: SEM> Measurement

The lithium-sulfur cell using the positive electrode according to Example 1 was charged and discharged 10 times, and the cell was separated. Thereafter, a central portion from the positive electrode was sampled by the following procedure, and a SEM photograph of the central portion is shown in FIG. 2. The central portion was a portion corresponding to 60% thereof, with the exception of right and left 20% portions, when the total longitudinal direction length of the positive electrode is seen as 100%, as shown in FIG. 3. In addition, the central portion did not include the folded portion where the electrode was wound. The central portion was controlled to have a horizontal length of 1 to 5 cm, and a vertical length of 1 to 5 cm.

The central portion of the electrode was washed with a dimethyoxethane solvent for 10 seconds and then dried at 40°C for 24 hours.

In FIG. 2, the V_2O_5 additive appeared in the form of oval particles rather than having a spherical shape. In this case, the particle size of the additive is determined as the longest

cross-section of the oval, and is 5,000 nm or less. In the figure, most particles have a diameter of 1,000 nm or less. This is believed to be because of the use of the ball in the slurry preparation. If the ball is not used in the slurry preparation, it is expected that the particle size of the additive will be maintained.

< Experiment 4: Measurement of battery performance>

Using positive electrodes according to each of Examples 1 to 6 and Comparative Example 1, pouch-type lithium-sulfur cells were fabricated by the following procedure. The size of each positive electrode was 25mm X 50mm. The cells were test cells with a higher capacity than a coin cell (capacity of 3-5mAh).

A tab was welded to each positive electrode and the resulting positive electrode was placed in a pouch. On the positive electrode, a separator was positioned. A tab-attached lithium foil was placed on the separator, and the pouch was sealed except for at an electrolyte inserting hole. 1M $LiN(SO_2CF_3)_2$ in dimethoxyethane/1,3-dioxolane (80/20 volume ratio) was injected into the pouch.

The cell was charged at 0.2C and discharged at 0.5C, the 1st capacity and cycle life for 100th cycles were measured, and the results are presented in Table 4. In addition, internal resistance of the battery and surface roughness Ra of the positive electrode are shown in Table 4.

Table 4

	Surface roughness (Ra in µm)	Internal resistance (Ω)	1st capacity (mAh/g)	Cycle life for 100th cycles (%)
Comparative Example 1	3.0	9.8	1200	60
Example 6	12.6	15.3	1053	55
Example 5	6.6	12.6	1125	58
Example 1	3.0	9.8	1215	76
Example 2	2.9	9.5	1230	85
Example 3	2.8	9.6	1250	88
Example 4	2.5	9.5	1280	90

It is shown in Table 4 that Examples 1 to 4 using V_2O_5 with the same or smaller particle size than the sulfur positive active material (5,000 nm) exhibited lower surface roughness than Comparative Example 1 without V_2O_5. Such a lower surface roughness renders a decrease in interfacial resistance, causing a decrease in internal resistance of the battery and an increase in 1st capacity and cycle life.

On the other hand, Examples 5 and 6 using V_2O_5 with a particle size larger than the sulfur positive active material (5,000 nm) exhibited greater surface roughness, which results in an increase in internal resistance and a decrease in capacity and cycle life.

Examples 7 to 11: Test for battery performance according to amount of added V_2O_5

Positive electrodes were produced by the same procedure as in Example 1, except that amounts of V_2O_5 with a particle size D (v, 50%) of 10 nm were changed as set forth in the following Table 5. The surface roughness of each positive electrode was measured, and the results are shown in Table 5. The result according to Example 4 with a particle size D (v, 50%) of 10 nm is also shown in Table 5.

Table 5

	Composition of positive electrode (weight ratio)	Surface roughness (Ra in μm)
Comparative Example 1	Sulfur/Conductive material/Binder (60/20/20)	3.0
Example 7	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=10nm) (60/20/20/2)	2.9
Example 8	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=10nm) (60/20/20/5)	2.8
Example 4	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=10nm) (60/20/20/10)	2.5
Example 9	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=10nm) (60/20/20/15)	2.4
Example 10	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=10nm) (60/20/20/20)	2.6
Example 11	Sulfur/Conductive material/Binder/V_2O_5(A: D(v, 50%)=10nm) (60/20/20/25)	2.5

Table 4 indicates that the same or smaller particle size of V_2O_5 than the positive active material decreases surface roughness when compared with Comparative Example 1 without V_2O_5.

< Experiment 5: Measurement of Battery Performance>

Using positive electrodes according to each of Examples 4 and 7 to 11, pouch-type lithium sulfur cells were fabricated by the same procedure as in Experiment 4. The cells were charged at 0.2C and discharged at 0.5C, the 1^{st} capacity and cycle life for the 100^{th} cycles were measured, and the results are presented in Table 6. In addition, internal resistance of each battery and surface roughness Ra of each positive electrode are shown in Table 6.

Table 6

	Surface roughness (Ra in μm)	Internal resistance (Ω)	1st capacity (mAh/g)	Cycle life for 100th cycles (%)
Comparative Example 1	3.0	9.8	1200	60
Example 7	2.9	9.7	1220	70
Example 8	2.8	9.5	1245	88
Example 4	2.5	9.5	1280	90
Example 9	2.4	9.3	1254	84
Example 10	2.6	9.4	1234	82
Example 11	2.5	9.3	1230	72

It is shown in Table 6 that Examples 4 and 7 to 11 using V_2O_5 with the same or smaller particle size than the sulfur positive active material (5,000 nm) exhibited lower surface roughness than Comparative Example 1 without V_2O_5. Such a lower surface roughness renders a decrease in interfacial resistance, causing a decrease in internal resistance of the battery. As a result, the 1st capacities in Examples 4 and 7 to 11 are slightly larger than that in Comparative Example 1, and the cycle life greatly increased by 5 to 20% when compared with Comparative Example 1. This is believed to result from higher ionic conductivity in 5 to 20wt% of V_2O_5, even though Examples 4 and 7 to 11 have similar surface roughness (See Table 2).

As a result, the V_2O_5 additive with the critical particle size increases ionic conductivity of the positive electrode and decreases surface roughness, thereby increasing capacity from 1200mAh to 1280mAh, and improving cycle life from 60% to 90%.

Experiment 6: Immersion of positive electrode in electrolyte

84 wt% of elemental sulfur (S_8), 12 wt% of a carbon conductive material, and 4 wt% of a styrene butadiene rubber binder were mixed, and V_2O_5 was added to the mixture in a water solvent to prepare positive active material slurries. The amounts of V_2O_5 were 2, 5, 10, 15, 20, 25, and 30 parts by weight based on 100 parts by weight of the mixture.

The slurries were coated on carbon-coated Al current collectors. The coated collectors were dried at room temperature for 2 hours, then dried at 80°C for 12 hours to produce positive electrodes.

The positive electrodes were cut with a width of 2.5cm and a length of 5.0cm.

As shown in FIG.1, 90ml of dimethylethane and dioxolane electrolytic solvents were respectively poured into 100ml beakers, and 1cm ends of the cut positive electrodes were immersed in the electrolytic solvents in the beakers for 1 minute. The height, which indicates a

degree to which the solvent is absorbed into the electrode and wicks up the electrode, was measured at room temperature under a normal atmosphere. The results are shown in Table 7.

Table 7

	Immersed height of dimethoxyethane (mm)	Immersed height of dioxolane (mm)
Sulfur/Conductive material/Binder (84/12/4)	2.0	1.0
Sulfur/Conductive material/Binder/V_2O_5 (84/12/4/2)	2.5	2.0
Sulfur/Conductive material/Binder/V_2O_5 (84/12/4/5)	4.0	3.0
Sulfur/Conductive material/Binder/V_2O_5 (84/12/4/10)	6.0	3.5
Sulfur/Conductive material/Binder/V_2O_5 (84/12/4/15)	8.0	6.0
Sulfur/Conductive material/Binder/V_2O_5 (84/12/4/20)	8.5	6.0
Sulfur/Conductive material/Binder/V_2O_5 (84/12/4/25)	8.5	6.0
Sulfur/Conductive material/Binder/V_2O_5 (84/12/4/30)	8.6	6.0

The results from Table 7 are believed to come about because the porosity of the positive electrodes increases by the addition of V_2O_5, which results in better immersion of the electrolyte. It is believed that such a better immersion allows retention of electrolyte in the positive electrode during the charge and the discharge, and prevents damage to the negative electrode due to the electrolyte, thereby improving cycle life.

Example 12

A ZrO_2 additive with a particle size D (v, 50%) of 3,000 nm, an elemental sulfur (S_8) positive active material, a carbon conductive material, and a polyethyleneoxide binder were mixed in an acetonitrile solvent in the weight ratio of 1 : 6 : 2 : 2 with a ball to prepare a positive active material slurry. The elemental sulfur (S_8) was obtained from pulverization with a zirconia ball in an isopropylalcohol solvent and drying, and it had a particle size D (v, 50%) of 5,000 nm.

The positive active material slurry was coated on a carbon-coated Al current collector to produce a positive electrode for a lithium-sulfur battery.

Example 13

ZrO_2 powder was pulverized in an isopropyl alcohol solvent with a zirconia ball for 1 hour, and the resulting material was dried at 80℃ to prepare a ZrO_2 additive with a particle size D (v, 50%) of 2,000 nm.

The ZrO_2 additive, an elemental sulfur (S_8) positive active material, a carbon conductive material, and a polyethyleneoxide binder were mixed in an acetonitrile solvent in the weight ratio of 1 : 6 : 2 : 2 with a ball to prepare a positive active material slurry. The elemental sulfur (S_8) was obtained from pulverization with a zirconia ball in an isopropylalcohol solvent and drying, and it had a particle size D (v, 50%) of 5,000 nm.

The positive active material slurry was coated on a carbon-coated Al current collector to produce a positive electrode for a lithium-sulfur battery.

Example 14

A positive electrode was produced by the same procedure as in Example 13, except that the pulverization step was performed for 6 hours to prepare a ZrO_2 additive with a particle size D (v, 50%) of 1,000 nm.

Example 15

A positive electrode was produced by the same procedure as in Example 13, except that the pulverization step was performed for 12 hours to prepare a ZrO_2 additive with a particle size D (v, 50%) of 100 nm.

Example 16

A positive electrode was produced by the same procedure as in Example 13, except that the pulverization step was performed for 24 hours to prepare a ZrO_2 additive with a particle size D (v, 50%) of 10 nm.

< Experiment 7: Measurement of ionic conductivity according to a particle size D (v, 50%) of ZrO_2>

Polyethylene oxide with a molecular weight of 5,000,000 was dissolved in acetonitrile, and a $LiN(SO_2CF_3)_2$ lithium salt was added thereto and dissolved therein until the mole ratio of ethylene oxide to Li reached 10 : 1. The ZrO_2 additives according to Examples 10 to 14 were respectively added to the resulting solution in an amount of 10 wt% based on the total amount of polyethylene oxide and the $LiN(SO_2CF_3)_2$ lithium salt, and they were shaken for 2 hours. The resulting solutions were cast to form polymer films, and ionic conductivity thereof was measured. The results are presented in Table 8.

Table 8

Type of polymer film	Ionic conductivity (S/cm) (room temperature)
PEO_{10}-$LiN(SO_2CF_3)_2$	9.6×10^{-7}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2(D(v, 50%)=3,000nm)	1.1×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2(D(v, 50%)=2,000nm)	2.7×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2(D(v, 50%)=1,000nm)	8.9×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2(D(v, 50%)=100nm)	3.5×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2(D(v, 50%)=10nm)	5.1×10^{-5}

As shown in Table 8, the addition of ZrO_2 increases ionic conductivity, and such an increase in ionic conductivity is further improved as the particle size of ZrO_2 becomes smaller. This believed to come about because the inorganic additive such as ZrO_2 prevents crystallization of the polymer.

Increases in ionic conductivity according to the amount of ZrO_2 were measured. ZrO_2 with a particle size D (v, 50%) of 10 nm was used. The results are presented in Table 9.

Table 9

Type of polymer film	Ionic conductivity (S/cm)(room temperature)
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2 (2 wt%)	1.2×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2 (5 wt%)	4.2×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2 (10 wt%)	5.1×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2 (15 wt%)	3.3×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2 (20 wt%)	2.1×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-ZrO_2 (25 wt%)	8.9×10^{-6}

It is evident from Table 9 that an amount of 5 to 15 wt% of ZrO_2 exhibited higher ionic conductivity.

These two test results indicate that ZrO_2 increases ionic conductivity and as the particle size of ZrO_2 decreases, ionic conductivity increases.

< Experiment 8: Measurement of surface roughness>

The surface roughness Ra of the positive electrodes according to Examples 12 to 16 and Comparative Example 1 were measured, and the results are shown in Table 10.

Table 10

	Composition of the positive electrode (weight ratio)	Surface roughness (Ra in μm)
Comparative Example 1	Sulfur/Conductive material/Binder (6/2/2)	3.0
Example 12	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=150000nm) (6/2/2/1)	2.9
Example 13	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=30000nm) (6/2/2/1)	2.6
Example 14	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=5000nm) (6/2/2/1)	2.5
Example 15	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=200nm) (6/2/2/1)	2.4
Example 16	Sulfur/Conductive material/Binder /ZrO_2(A: D(v, 50%)=50nm) (6/2/2/1)	2.3

In Table 10, Ra indicates the arithmetic mean of each peak (between highest and lowest peaks), and the lower Ra indicates a more uniform surface. It is evident from Table 10 that Comparative Example 1 without ZrO_2 exhibited poor uniformity (unevenness), whereas Examples 12 to 16 with ZrO_2 exhibited good uniformity.

< Experiment 9: Measurement of battery performance>

Using positive electrodes according to each of Examples 12 to 16 and Comparative Example 1, pouch-type lithium-sulfur cells were fabricated by the following procedure. The size of each positive electrode was 25mm X 50mm. The cells were test cells with a higher capacity than a coin cell (capacity of 3-5mAh).

A tab was welded to each positive electrode, and the resulting positive electrode was placed in a pouch. On the positive electrode, a separator was positioned. A tab-attached lithium foil was placed on the separator, and the pouch was sealed except for an electrolyte inserting hole. 1M $LiN(SO_2CF_3)_2$ in dimethoxyethane/1,3-dioxolane (80/20 volume ratio) was injected into the pouch.

Each cell was charged at 0.2C and discharged at 0.5C, and the 1^{st} capacity and cycle life for 100^{th} cycles were measured, and the results are presented in Table 11. In addition, internal resistance of each battery and surface roughness Ra of each positive electrode are shown in Table 11.

Table 11

	Surface roughness (Ra in ㎛)	Internal resistance (Ω)	1st capacity (mAh/g)	Cycle life for 100th cycles (%)
Comparative Example 1	3.0	9.8	1200	60
Example 12	2.9	9.8	1050	65
Example 13	2.6	9.6	1122	70
Example 14	2.5	9.5	1233	86
Example 15	2.4	9.6	1252	87
Example 16	2.3	9.5	1288	91

It is shown in Table 11 that Examples 12 to 16 using ZrO_2 exhibited lower surface roughness than Comparative Example 1 without ZrO_2. Such a lower surface roughness renders a decrease in interfacial resistance, causing a decrease in internal resistance of the battery and increases in 1st capacity and cycle life.

Examples 17 to 21: Test for battery performance according to amount of added ZrO_2

Positive electrodes for a lithium-sulfur cell were produced by the same procedure as in Example 1, except that the amounts of ZrO_2 with a particle size D (v, 50%) of 10 nm were varied as set forth in the following Table 12. The surface roughness of each positive electrode was measured, and the results are shown in Table 12. The result according to Example 16 with a particle size D (v, 50%) of 10 nm is also shown in Table 12.

Table 12

	Composition of positive electrode (weight ratio)	Surface roughness (Ra in ㎛)
Comparative Example 1	Sulfur/Conductive material/Binder (60/20/20)	3.0
Example 17	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=10nm) (60/20/20/2)	2.9
Example 18	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=10nm) (60/20/20/5)	2.8
Example 16	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=10nm) (60/20/20/10)	2.5
Example 19	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=10nm) (60/20/20/15)	2.4
Example 20	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=10nm) (60/20/20/20)	2.6
Example 21	Sulfur/Conductive material/Binder/ZrO_2(A: D(v, 50%)=10nm) (60/20/20/25)	2.5

Table 12 indicates that the same or smaller particle size of ZrO_2 than the positive active material decreases surface roughness when compared with Comparative Example 1 without ZrO_2.

< Experiment 10: Measurement of Battery Performance>

Using positive electrodes according to each of Examples 16 to 21, pouch-type lithium sulfur cells were fabricated by the same procedure as in Experiment 8. The cells were charged at 0.2C and discharged at 0.5C, and the 1st capacity and cycle life for 100th cycles were measured, and the results are presented in Table 13. In addition, internal resistance of each battery and surface roughness Ra of each positive electrode are shown in Table 13.

Table 13

	Surface roughness (Ra in μm)	Internal resistance (Ω)	1st capacity (mAh/g)	Cycle life for 100th cycles (%)
Comparative Example 1	3.0	9.8	1200	60
Example 17	2.9	9.6	1225	71
Example 18	2.7	9.5	1249	87
Example 16	2.3	9.5	1288	91
Example 19	2.4	9.4	1258	85
Example 20	2.5	9.4	1233	81
Example 21	2.5	9.3	1232	74

It is shown in Table 13 that Examples 16 to 21 using ZrO_2 exhibited lower surface roughness than Comparative Example 1 without ZrO_2. Such lower surface roughness renders a decrease in interfacial resistance between the positive electrode and the separator, causing a decrease in internal resistance of the battery. As a result, the 1st capacities in Examples 16 to 21 are slightly larger than that in Comparative Example 1, and the cycle life greatly increased by 5 to 20% when compared with Comparative Example 1. This result is believed to come about from the higher ionic conductivity in 5 to 20wt% of V_2O_5 even though Examples 16 to 21 have similar surface roughness (See Table 8).

As a result, the ZrO_2 additive with the critical particle size increases ionic conductivity of the positive electrode and decreases surface roughness, thereby increasing capacity from 1200mAh to 1288mAh, and improving cycle life from 60% to 91%.

Example 22

A TiS_2 additive with a particle size D (v, 50%) of 75,000 nm, an elemental sulfur (S_8) positive active material, a carbon conductive material and a polyethyleneoxide binder were mixed in an acetonitrile solvent in the weight ratio of 1 : 6 : 2 : 2 with a ball to prepare a positive

active material slurry. The elemental sulfur (S_8) was obtained from pulverization with a zirconia ball in an isopropylalcohol solvent and drying, and it had a particle size D (v, 50%) of 5,000 nm.

The positive active material slurry was coated on a carbon-coated Al current collector to produce a positive electrode for a lithium-sulfur battery.

Example 23

TiS_2 powder was pulverized in an isopropyl alcohol solvent with a zirconia ball for 1 hour, and the resulting material was dried at 80℃ to prepare a TiS_2 additive with a particle size D (v, 50%) of 20,000 nm.

The TiS_2 additive, an elemental sulfur (S_8) positive active material, a carbon conductive material, and a polyethyleneoxide binder were mixed in an acetonitrile solvent in the weight ratio of 1 : 6 : 2 : 2 with a ball to prepare a positive active material slurry. The elemental sulfur (S_8) was obtained from pulverization with a zirconia ball in an isopropylalcohol solvent and drying, and it had a particle size D (v, 50%) of 5,000 nm.

The positive active material slurry was coated on a carbon-coated Al current collector to produce a positive electrode for a lithium-sulfur battery.

Example 24

A positive electrode was produced by the same procedure as in Example 23, except that the pulverization step was performed for 3 hours to prepare a TiS_2 additive with a particle size D (v, 50%) of 5,000 nm.

Example 25

A positive electrode was produced by the same procedure as in Example 23, except that the pulverization step was performed for 6 hours to prepare a TiS_2 additive with a particle size D (v, 50%) of 1,000 nm.

Example 26

A positive electrode was produced by the same procedure as in Example 23 except that a pulverization step was performed for 12 hours to prepare a TiS_2 additive with a particle size D (v, 50%) of 100 nm.

Example 27

A positive electrode was produced by the same procedure as in Example 23, except that the pulverization step was performed for 24 hours to prepare a TiS_2 additive with a particle size D (v, 50%) of 10 nm.

< Experiment 11: Measurement of ionic conductivity according to a particle size D (v, 50%) of TiS_2>

Polyethylene oxide with a molecular weight of 5,000,000 was dissolved in acetonitrile, and a $LiN(SO_2CF_3)_2$ lithium salt was added thereto and dissolved therein until the mole ratio of ethylene oxide to Li reached 10 : 1. The TiS_2 additives according to Examples 20 to 25 were added to the resulting solution in an amount of 10 wt% based on the total amount of polyethylene oxide and the $LiN(SO_2CF_3)_2$ lithium salt, and they were shaken for 2 hours. The resulting solutions were cast to form polymer films, and the ionic conductivity of each was measured. The results are presented in Table 14.

Table 14

Type of polymer film	Ionic conductivity (S/cm) (room temperature)
PEO_{10}-$LiN(SO_2CF_3)_2$	9.6×10^{-7}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(D(v, 50%)=75,000nm)	1.1×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(D(v, 50%)=20,000nm)	2.7×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(D(v, 50%)=5,000nm)	5.0×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(D(v, 50%)=1,000nm)	8.9×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(D(v, 50%)=100nm)	3.5×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(D(v, 50%)=10nm)	5.1×10^{-5}

As shown in Table 14, the addition of TiS_2 increases ionic conductivity, and such an increase in ionic conductivity is improved as the particle size of TiS_2 becomes smaller. This is believed to be because an inorganic additive such as TiS_2 prevents crystallization of the polymer.

The increases in ionic conductivity according to the amount of TiS_2 were measured. TiS_2 with a particle size D (v, 50%) of 10 nm was used. The results are presented in Table 15.

Table 15

Type of polymer film	Ionic conductivity (S/cm)(room temperature)
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(2 wt%)	1.2×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(5 wt%)	4.4×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(10 wt%)	5.1×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(15 wt%)	3.2×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(20 wt%)	2.2×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-TiS_2(25 wt%)	8.6×10^{-6}

It is evident from Table 15 that an amount of 5 to 15 wt% of TiS_2 exhibited higher ionic conductivity.

These two test results indicate that TiS_2 increases ionic conductivity, and as the particle size of TiS_2 decreases, ionic conductivity increases.

< Experiment 12: Measurement of surface roughness>

The surface roughness Ra of each positive electrode according to Examples 22 to 27 and Comparative Example 1 were measured, and the results are shown in Table 16.

Table 16

	Composition of the positive electrode (weight ratio)	Surface roughness (Ra in μm)
Comparative Example 1	Sulfur/Conductive material/Binder (6/2/2)	3.0
Example 22	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=75,000nm) (6/2/2/1)	7.6
Example 23	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=20,000nm) (6/2/2/1)	5.4
Example 24	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=5,000nm) (6/2/2/1)	3.0
Example 25	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=1,000nm) (6/2/2/1)	2.6
Example 26	Sulfur/Conductive material/Binder /TiS_2(A: D(v, 50%)=100nm) (6/2/2/1)	2.4
Example 27	Sulfur/Conductive material/Binder /TiS_2(A: D(v, 50%)=10nm) (6/2/2/1)	2.3

In Table 16, Ra indicates the arithmetic mean of each peak (between highest and lowest peaks), and the lower Ra indicates a more uniform surface. It is evident from Table 16 that Examples 24 to 27 exhibited improved surface roughness.

< Experiment 13: Measurement of battery performance>

Using positive electrodes according to each of Examples 22 to 27 and Comparative Example 1, pouch-type lithium-sulfur cells were fabricated by the following procedure. The size of each positive electrode was 25mm X 50mm. The cells were test cells with a higher capacity than a coin cell (capacity of 3-5mAh).

A tab was welded to each positive electrode, and the resulting positive electrode was placed in a pouch. On the positive electrode, a separator was positioned. A tab-attached lithium foil was placed on the separator, and the pouch was sealed except for an electrolyte inserting hole. 1M $LiN(SO_2CF_3)_2$ in dimethoxyethane/1,3-dioxolane (80/20 volume ratio) was injected into the pouch.

The cells were charged at 0.2C and discharged at 0.5C, the 1st capacity and cycle life for 100th cycles were measured, and the results are presented in Table 17. In addition, internal resistance of the batteries and surface roughness Ra of the positive electrodes are shown in Table 17.

Table 17

	Surface roughness (Ra in μm)	Internal resistance (Ω)	1st capacity (mAh/g)	Cycle life for 100th cycles (%)
Comparative Example 1	3.0	9.8	1200	60
Example 22	7.6	12.3	1175	63
Example 23	5.4	10.5	1185	74
Example 24	3.0	9.8	1211	73
Example 25	2.6	9.5	1246	83
Example 26	2.4	9.6	1254	88
Example 27	2.3	9.4	1279	90

It is shown in Table 17 that Examples 22 to 27 using TiS_2 exhibited lower surface roughness than Comparative Example 1 without TiS_2. Such a lower surface roughness renders a decrease in interfacial resistance, causing a decrease in internal resistance of the battery and an increase in 1st capacity and cycle life.

Examples 28 to 32: Test for battery performance according to amount of added TiS_2

Positive electrodes for a lithium-sulfur cell were produced by the same procedure as in Example 22, except that amounts of TiS_2 with a particle size D (v, 50%) of 10 nm were varied as set forth in the following Table 18. The surface roughness of each positive electrode was measured, and the results are shown in Table 18. The result according to Example 27 with a particle size D (v, 50%) of 10 nm is also shown in Table 18.

Table 18

	Composition of positive electrode (weight ratio)	Surface roughness (Ra in µm)
Comparative Example 1	Sulfur/Conductive material/Binder (60/20/20)	3.0
Example 28	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=10nm) (60/20/20/2)	2.9
Example 29	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=10nm) (60/20/20/5)	2.7
Example 27	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=10nm) (60/20/20/10)	2.3
Example 30	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=10nm) (60/20/20/15)	2.2
Example 31	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=10nm) (60/20/20/20)	2.3
Example 32	Sulfur/Conductive material/Binder/TiS_2(A: D(v, 50%)=10nm) (60/20/20/25)	2.2

Table 18 indicates that a particle size of TiS_2 less than or equal to that of the positive active material decreases surface roughness when compared with Comparative Example 1 without TiS_2.

< Experiment 14: Measurement of Battery Performance>

Using positive electrodes according to each of Examples 27 to 32, pouch-type lithium sulfur cells were fabricated by the same procedure as in Experiment 13. The cells were charged at 0.2C and discharged at 0.5C, the 1st capacity and cycle life for 100th cycles were measured, and the results are presented in Table 19. In addition, internal resistance of each battery and surface roughness Ra of each positive electrode are shown in Table 19.

Table 19

	Surface roughness (Ra in µm)	Internal resistance (Ω)	1st capacity (mAh/g)	Cycle life for 100th cycles (%)
Comparative Example 1	3.0	9.8	1200	60
Example 28	2.9	9.7	1228	70
Example 29	2.7	9.6	1244	85
Example 27	2.3	9.4	1279	90
Example 30	2.2	9.3	1250	88
Example 31	2.3	9.4	1237	82
Example 32	2.2	9.3	1229	72

It is shown in Table 19 that Examples 27 to 31 using TiS_2 exhibited lower surface roughness than Comparative Example 1 without TiS_2. Such a lower surface roughness renders a decrease in interfacial resistance between the positive electrode and the separator, causing a decrease in internal resistance of the battery. As a result, the 1st capacities in Examples 16 to 21 are slightly larger than that of Comparative Example 1, and the cycle life greatly increased by 5 to 20% when compared with Comparative Example 1. This result is believed to come about because of the higher ionic conductivity with 5 to 20wt% of TiS_2, even though Examples 27 to 32 have similar surface roughness (See Table 15).

As a result, the TiS_2 additive with the critical particle size increases ionic conductivity of the positive electrode and decreases surface roughness, thereby increasing capacity from 1200mAh to 1279mAh, and improving cycle life from 60% to 90%.

Example 33

Al_2O_3 powder was pulverized in an isopropyl alcohol solvent with a zirconia ball for 1 hour, and the resulting material was dried at 80°C to prepare an Al_2O_3 additive with a particle size D (v, 50%) of 35,000 nm.

The Al_2O_3 additive, an elemental sulfur (S_8) positive active material, a carbon conductive material, and a polyethyleneoxide binder were mixed in an acetonitrile solvent in the weight ratio of 1 : 6 : 2 : 2 with a ball to prepare a positive active material slurry. The elemental sulfur (S_8) was obtained from pulverization with a zirconia ball in isopropylalcohol solvent, and drying, and it had a particle size D (v, 50%) of 5,000 nm.

The positive active material slurry was coated on a carbon-coated Al current collector to produce a positive electrode for a lithium-sulfur battery.

Example 34

A positive electrode was produced by the same procedure as in Example 33, except that the pulverization step was performed for 3 hours to prepare an Al_2O_3 additive with a particle size D (v, 50%) of 5,000 nm.

Example 35

A positive electrode was produced by the same procedure as in Example 33, except that the pulverization step was performed for 6 hours to prepare an Al_2O_3 additive with a particle size D (v, 50%) of 200 nm.

Example 36

A positive electrode was produced by the same procedure as in Example 33, except that the pulverization step was performed for 12 hours to prepare an Al_2O_3 additive with a particle size D (v, 50%) of 50 nm.

Example 37

A positive electrode was produced by the same procedure as in Example 33, except that the pulverization step was performed for 24 hours to prepare an Al_2O_3 additive with a particle size D (v, 50%) of 6 nm.

Example 38

A positive electrode was produced by the same procedure as in Example 33, except that the pulverization step was performed for 48 hours to prepare an Al_2O_3 additive with a particle size D (v, 50%) of 5.8 nm.

Example 39

A positive electrode was produced by the same procedure as in Example 33, except that a V_2O_5 additive with a particle size D (v, 50%) of 109,000 nm without a pulverization step was used.

< Experiment 1: Measurement of ionic conductivity according to a particle size D (v, 50%) of Al_2O_3>

Polyethylene oxide with a molecular weight of 5,000,000 was dissolved in acetonitrile, and a $LiN(SO_2CF_3)_2$ lithium salt was added thereto and dissolved therein until the mole ratio of ethylene oxide to Li reached 10 : 1. An Al_2O_3 additive according to one of Examples 33 to 39 and Comparative Example 1 was added to the resulting solution in the amount of 10 wt% of the total amount of polyethylene oxide and the $LiN(SO_2CF_3)_2$ lithium salt, and they were shaken for 2 hours. The resulting solution was cast to form a polymer film, and the ionic conductivity thereof was measured. The results are presented in Table 20.

Table 20

Type of polymer film	Ionic conductivity (S/cm) (room temperature)
PEO_{10}-$LiN(SO_2CF_3)_2$	9.6×10^{-7}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3(D(v, 50%)=109,000nm)	1.5×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3(D(v, 50%)=35,000nm)	2.7×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3(D(v, 50%)=5,000nm)	3.7×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3(D(v, 50%)=200nm)	7.6×10^{-6}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3(D(v, 50%)=50nm)	4.2×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3(D(v, 50%)=6nm)	5.0×10^{-5}

As shown in Table 20, the addition of Al_2O_3 increases ionic conductivity, and such an increase in ionic conductivity is improved as the particle size of Al_2O_3 decreases. This is believed to be because the inorganic additive such as Al_2O_3 prevents the crystallization of the polymer.

The increases in ionic conductivity according to the amount of Al_2O_3 were measured. Al_2O_3 with a particle size D (v, 50%) of 6 nm was used. The results are presented in Table 21.

Table 21

Type of polymer film	Ionic conductivity (S/cm)(room temperature)
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3 (2 wt%)	1.2×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3 (5 wt%)	4.1×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3 (10 wt%)	5.0×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3 (15 wt%)	3.8×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3 (20 wt%)	2.2×10^{-5}
PEO_{10}-$LiN(SO_2CF_3)_2$-Al_2O_3 (25 wt%)	7.0×10^{-6}

It is evident from Table 21 that an amount of 5 to 15 wt% of Al_2O_3 exhibited higher ionic conductivity.

These two test results indicate that Al_2O_3 increases ionic conductivity and as the particle size of Al_2O_3 decreases, ionic conductivity increases.

< Experiment 16: Measurement of surface roughness>

The surface roughness Ra of each positive electrode according to Examples 33 to 39 and Comparative Example 1 was measured, and the results are shown in Table 22.

Table 22

	Composition of the positive electrode (weight ratio)	Surface roughness (Ra in ㎛)
Comparative Example 1	Sulfur/Conductive material/Binder (6/2/2)	3.0
Example 39	Sulfur/Conductive material/Binder/Al_2O_3(D(v, 50%)=109,000nm) (6/2/2/1)	11.5
Example 33	Sulfur/Conductive material/Binder/Al_2O_3 (D(v, 50%)=35,000nm) (6/2/2/1)	6.2
Example 34	Sulfur/Conductive material/Binder/Al_2O_3 (D(v, 50%)=5,000nm) (6/2/2/1)	3.0
Example 35	Sulfur/Conductive material/Binder/Al_2O_3 (D(v, 50%)=200nm) (6/2/2/1)	2.8
Example 36	Sulfur/Conductive material/Binder /Al_2O_3 (D(v, 50%)=50nm) (6/2/2/1)	2.6
Example 37	Sulfur/Conductive material/Binder /Al_2O_3 (D(v, 50%)=6nm) (6/2/2/1)	2.3

In Table 22, Ra indicates the arithmetic mean of each peak (between highest and lowest peaks), and the lower Ra indicates a more uniform surface. It is evident from Table 22 that Examples 33 and 39 with a particle size of Al_2O_3 larger than the sulfur active material (5,000nm) exhibited poorer uniformity (unevenness and roughness) than Comparative Example 1 without Al_2O_3, and Examples 34 to 37 with a smaller or the same particle size of Al_2O_3 as the active material exhibited the same or better uniformity.

< Experiment 17: Measurement of battery performance>

Using positive electrodes according to each of Examples 33 to 39 and Comparative Example 1, pouch-type lithium-sulfur cells were fabricated by the following procedure. The size of each positive electrode was 25mm X 50mm. The cells were test cells with a higher capacity than a coin cell (capacity of 3-5mAh).

A tab was welded to each positive electrode, and the resulting positive electrode was placed in a pouch. On the positive electrode, a separator was positioned. A tab-attached lithium foil was placed on the separator, and the pouch was sealed except for an electrolyte inserting hole. 1M $LiN(SO_2CF_3)_2$ in dimethoxyethane/1,3-dioxolane (80/20 volume ratio) was injected into the pouch.

The cells were charged at 0.2C and discharged at 0.5C, and the 1st capacity and cycle life for the 100th cycles were measured, and the results are presented in Table 23. In addition, internal resistance of each battery and surface roughness Ra of each positive electrode are shown in Table 23.

Table 23

	Surface roughness (Ra in µm)	Internal resistance (Ω)	1^{st} capacity (mAh/g)	Cycle life for 100th cycles (%)
Comparative Example 1	3.0	9.8	1200	60
Example 39	11.5	14.5	1188	62
Example 33	6.2	11.5	1165	65
Example 34	3.0	9.8	1210	75
Example 35	2.8	9.5	1236	85
Example 36	2.6	9.6	1254	89
Example 37	2.3	9.4	1289	91

It is shown in Table 23 that Examples 34 to 38 using Al_2O_3 with the same or smaller particle size than the sulfur positive active material (5,000 nm) exhibited lower surface roughness than Comparative Example 1 without Al_2O_3. Such a lower surface roughness renders a decrease in interfacial resistance, causing a decrease in internal resistance of the battery and an increase in 1^{st} capacity and cycle life.

On the other hand, Examples 33 and 39 using Al_2O_3 with a particle size larger than the sulfur positive active material (5,000 nm) exhibited more surface roughness, which results in an increase in internal resistance and a decrease in capacity and cycle life.

Examples 38 to 42: Test for battery performance according to amount of added V_2O_5

Positive electrodes were produced by the same procedure as in Example 33, except that amounts of Al_2O_3 with a particle size D (v, 50%) of 6 nm were varied as set forth in the following Table 24. The surface roughness of each positive electrode was measured, and the results are shown in Table 24. The result according to Example 36 with a particle size D (v, 50%) of 6 nm is also shown in Table 24.

Table 24

	Composition of positive electrode (weight ratio)	Surface roughness (Ra in µm)
Comparative Example 1	Sulfur/Conductive material/Binder (60/20/20)	3.0
Example 38	Sulfur/Conductive material/Binder/Al_2O_3(A: D(v, 50%)=6nm) (60/20/20/2)	2.8
Example 39	Sulfur/Conductive material/Binder/Al_2O_3(A: D(v, 50%)=6nm) (60/20/20/5)	2.8
Example 36	Sulfur/Conductive material/Binder/Al_2O_3(A: D(v, 50%)=6nm) (60/20/20/10)	2.3
Example 40	Sulfur/Conductive material/Binder/Al_2O_3(A: D(v, 50%)=6nm) (60/20/20/15)	2.2
Example 41	Sulfur/Conductive material/Binder/Al_2O_3(A: D(v, 50%)=6nm) (60/20/20/20)	2.4
Example 42	Sulfur/Conductive material/Binder/Al_2O_3(A: D(v, 50%)=6nm) (60/20/20/25)	2.3

Table 24 indicates that the same or smaller particle size of Al_2O_3 than the positive active material decreases surface roughness when compared with Comparative Example 1 without Al_2O_3.

< Experiment 18: Measurement of Battery Performance>

Using positive electrode according to each of Examples 36 and 38 to 42, pouch-type lithium sulfur cells were fabricated by the same procedure as in Experiment 17. The cells were charged at 0.2C and discharged at 0.5C, the 1st capacity and cycle life for 100th cycles were measured, and the results are presented in Table 25. In addition, internal resistance of each battery and surface roughness Ra of each positive electrode are shown in Table 25.

Table 25

	Surface roughness (Ra in µm)	Internal resistance (Ω)	1st capacity (mAh/g)	Cycle life for 100th cycles (%)
Comparative Example 1	3.0	9.8	1200	60
Example 38	2.8	9.6	1218	71
Example 39	2.8	9.6	1240	87
Example 36	2.3	9.4	1289	91
Example 40	2.2	9.3	1255	88
Example 41	2.4	9.5	1239	86
Example 42	2.3	9.4	1231	75

It is shown in Table 25 that Examples 36 and 38 to 42 using Al_2O_3 with the same or smaller particle size than the sulfur positive active material (5,000 nm) exhibited lower surface

roughness than Comparative Example 1 without Al_2O_3. Such a lower surface roughness renders a decrease in interfacial resistance, causing a decrease in internal resistance of the battery. As a result, the 1st capacities in Examples 36 and 38 to 42 are slightly larger than that in Comparative Example 1, and the cycle life greatly increases by 5 to 20% when compared to Comparative Example 1. This result is believed to come about from higher ionic conductivity in 5 to 20wt% of Al_2O_3 even though Examples 36 and 38 to 42 have similar surface roughness (See Table 21).

As a result, the Al_2O_3 additive with the critical particle size increases ionic conductivity of the positive electrode and decreases surface roughness, thereby increasing capacity from 1200mAh to 1289mAh, and improving cycle life from 60% to 91%.

While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

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